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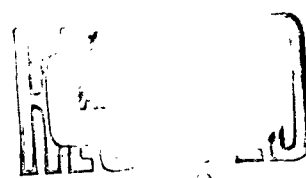
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ELECTROFORMING REFRACTORY METAL ALLOYS



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**ERR-FW-217**  
**Structural**

**ELECTROFORMING REFRACTORY METAL ALLOYS**

by

**E. W. Turns and J. F. Hildebrand**

**31 December 1962**

**RESEARCH & ENGINEERING DEPARTMENTS**

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**GENERAL DYNAMICS | FORT WORTH**

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## SUMMARY

The process of electroforming has certain advantages and in some cases unique capabilities over all other means of product fabrication. Its strongest virtue is that of producing a variety of complex configurations impossible to produce in any other manner. At least one side adjoining the mandrel reproduces in exact detail the desired surface. Also the products - electroforms - are usually compact, dense, non-porous materials.

At present the electroforming industry works primarily with nickel, copper, and silver. While many useful products are produced from those materials, their properties in aerospace environments are somewhat inadequate. Electroforming materials are needed for applications requiring high tensile strength, high temperature air oxidation resistance, corrosion resistance, high hardness and wear resistance.

Experiments to evaluate potential electroforming materials were conducted according to a three-phase program. First, twenty-six solutions capable of electrodepositing alloys were prepared, electroreduced, and the products examined. These solutions and products were examined for product uniformity, control of alloy ingredient and solution stability.

In the second phase three solutions were selected from the screening test. Limited experiments were conducted with a nickel manganese alloy, while more extensive experiments were

performed with a Co-W and a Co-W-Ni solution. In the third phase the latter two were adapted and improved to function as true electroforming solutions. Test specimens of a cobalt-nickel-tungsten alloy were prepared and tested to obtain tensile strength and hardness data. The tensile strength for this material was 49,600 psi, while the hardness was approximately Rockwell C 50.

Specimens of a cobalt-tungsten alloy were prepared and subjected to the following tests: hardness, tensile strength, melting point, Taber abrasion wear resistance, 1800°F air oxidation resistance and salt spray accelerated corrosion resistance. The cobalt-tungsten electroforms had the following physical properties: (1) tensile strength as high as 131,000 psi, (2) hardness of Rockwell C 52, (3) Taber abrasion resistance substantially superior to electroformed nickel or comparable to 321 stainless steel, (4) good salt spray corrosion resistance, (5) fair 1800°F air oxidation resistance.

This is a composite report for all Engineering Research on electroforming conducted during 1961 and 1962.

#### FOREWORD

The authors acknowledge support from Mr. T. E. Coyle of GD/FW Materials and Process Group. He was especially helpful in the selection of addition agents and in program guidance. Mr. C. E. Miller of GD/FW Materials Laboratory performed all of the analytical work in controlling deposit composition and also to verify final deposit composition.

#### OBJECTIVE

The objective of this program was to investigate electroforming processes, to adapt solutions to alloy deposition, and to test the resultant electroforms as potential aerospace materials.

## ELECTROFORMING REFRACTORY METAL ALLOYS

### INTRODUCTION

A study of the history of electroforming reveals that in 1838, Professor Jacobi of St. Petersburg, Russia, presented a paper on metallic coating processes for plaster or wax molds. At first this process was called galvanoplasty. A year later in England, F. T. Spencer and C. J. Jordan described a similar process. Thus, Professor Jacobi is generally considered to be the originator of electroforming.

Adaptation of these discoveries to modern production methods began in the printing and engraving industry. In the last two decades electroforming has grown to the production of many articles. Today the electroforming process makes many articles e.g., reflectors, phonograph record molds, aircraft pitot tubes, fountain pen caps, musical instruments, "flash" cards, embossing rollers and electronic wave guides. Although electroforming costs may be high, they are not prohibitive when a specifically desired shape or configuration cannot be produced by other manufacturing techniques.

Industrial electroforms are produced primarily from copper and nickel and occasionally from silver, cobalt, and chromium. While these metals are quite adequate for their present use, they are totally inadequate for many applications in the aerospace industry.

Specifically, electroformed metals are needed in two related and usually combined categories—ductile high strength (200 ksi plus tensile) materials and high temperature air oxidation resistance. Many of the refractory metals such as hafnium, zirconium, tantalum, tungsten, and molybdenum in the electroformed state would be useful in these problem areas, but unfortunately there are no production methods for electrodepositing these metals. Various factors prevent their electrodeposition in the elemental state. Some of them have electrodeposition potentials considerably greater than water, some are so active chemically they immediately oxidize when electroreduced to the elemental state. Consequently, it is conceded that electrodeposition of these desirable metals, in single element state, at present is not possible from aqueous media.

However, several of the refractory metals have been co-deposited in alloy form. In 1931 Fink and Jones<sup>1</sup> produced alloys of tungsten and tantalum; some of their thin films contained as much as 50% tungsten. Soon afterwards, in 1936 to 1940, Armstrong and Menefee<sup>2</sup> performed experiments on tungsten alloys. They were granted patents on methods, products, anodes, etc. Principally, their solutions were complex acid fluoride solutions which formed  $WO_2F_2$ . During this same period, in 1936, L. N. Goltz and V. N. Kharlamov<sup>3</sup> produced tungsten-nickel alloys from ammoniacal solutions. In 1937, Holt<sup>4</sup> discussed tungsten alloy deposits from alkaline tungsten baths. Later in 1943 Holt, Black and Hoglund<sup>5</sup> were

successful in depositing cobalt-tungsten from an alloy bath. Nickel-tungsten alloys were produced from ammoniacal-citrate baths by Holt and Vaaler<sup>6</sup> in 1946. A year later, Brenner, Burkhead, and Seegmiller<sup>7</sup> developed methods for producing tungsten from ammoniacal-citrate and tartrate solutions. In 1957, work in the Soviet Union was reported by Frantsevich-Zubludovskaya and Zayats<sup>8</sup>. Their primary efforts were with nickel-tungsten deposits.

In our search for a high strength, oxidation resistant electroforming material the alloy electrodeposits described above looked promising. Alloying has been employed extensively to extend the usefulness of metallic elements. It was postulated that alloys utilizing refractory metals would have the following desirable attributes.

1. Improved (superior to Ni or Co) high temperature air oxidation resistance.
2. Improved (superior to Ni or Co) high temperature structural strength.
3. Variable, versatile heat treatable alloy composition.

In exploring the feasibility of alloy electroforming, three related laboratory research programs were conducted. These programs were: (1) Experimental electrodeposition of various alloys, (2) Laboratory preparation and testing of Co-Ni-W alloy, (3) Laboratory preparation and testing of Co-W alloys.

## TECHNICAL ASPECTS OF ALLOY ELECTROFORMING

Several aspects relevant to alloy electroforming must be understood and placed under control before truly successful alloy electroforming can be accomplished. These various aspects are listed below with technical explanations as to importance, practicality, etc.

### I. Factors Affecting Control of Alloy Composition in Electroforming -

#### A. Electrodeposition Potential:

"The same principles apply to, and the same few variables control, both alloy and single metal deposition. In order to codeposit two or more metals, the variables must be combined in a way that causes the metals to codeposit at the same potential. The electrodeposition potential of a metal or alloy is determined by the activities of cations and anions in the cathode 'film' and by temperature of the solution. The activities are functions of the ion concentrations which, in the cathode film, are determined by the rate of deposition, by the ion concentration in the bath and by the rates of diffusion of the ions involved. Thus there is a different 'table' of deposition (and of static equilibrium) potentials for metals, depending on the chemical nature of the electrolytic solutions. There is no single, fixed set of values for static and

deposition potentials of metals that is universal for all condition. This situation makes codeposition of metals not only possible but practical."<sup>9</sup>

To calculate this electrodeposition potential the Parks and LeBaron<sup>10</sup> equation may be used. In this equation the limiting concentration of the second metal in the bath at which pure second metal will deposit is shown as a function of the valences of the two metals, the difference in single deposition potentials, the equivalent weights of the co-depositing metals, and the cathode current density, where mono and bivalent metals are involved in acid baths. The equation is stated as follows:

$$L = \frac{aZ_1^2 - bZ_2^2}{Z_2^2 + cZ_1^2} \cdot \frac{1^{1/2}}{N} \cdot \frac{E_L}{E_H} \cdot \text{Log c.d.}$$

$$L = \frac{C_1}{C_2} \text{ where } C_1 \text{ is the concentration of cation of}$$

lower cathode potential at the limit of codeposition.  $Z_1$  is the valence of ions of lower cathode potential;  $Z_2$  is the valence of ions of higher cathode potential.  $N$  is the difference in cathode potentials of the pure metals at the given cathode current density.  $E_L$  is the equivalent weight of metal of lower cathode potential;  $E_H$  is the equivalent weight of metal of higher cathode potential. c.d. is the cathode current density (ma/sq cm).  $a$ ,  $b$ , and  $c$  are constants which Parks and LeBaron empirically

evaluated from data on several combinations of co-deposited metals.

Another method for determining the electrodeposition potential is by empirical means. Basically, this involves comparing and adjusting desired metal salt concentrations and current densities to results of analysis for deposit composition. In any case an increase in current density usually increases the proportion of the less noble metal in the alloy electroform.

B. Solution Composition:

Another important factor that influences alloy electrodeposition is the solution metal-ion concentrations. The metal-ion concentration for each metal in the electroformed alloy must be carefully controlled. With binary and ternary deposits it is virtually impossible to introduce an alloy anode that will corrode and replenish the desired metal ion concentration exactly. Actually, it is more practical to replenish the major elements via anode corrosion and add constantly, or at frequent intervals, the minor ingredient metal salt. Of course one must also have an otherwise balanced bath, buffered, conductive, etc.

C. Temperature:

In alloy electroforming the highest practical temperature should be selected. Thus the electroforming rate (microinches/hour) will be highest, which will tend to make the process more economical. An increase in

temperature will usually increase the proportion of the more noble metal in the alloy electroform.

D. pH:

Control of the solution pH is most important and requires continuous monitoring in order to maintain an adequate metal-ion concentration and to assure the desired physical property of the deposit.

II. Improving the Mechanical Properties of the Alloy Electroform

Electroforms, particularly those containing W, are brittle in the as-deposited condition. This deficiency may be minimized by control of the plating procedures and by selected heat treatments. The cobalt-tungsten and cobalt-nickel-tungsten phase diagrams indicate that some of these alloys may be solution heat treated to produce primarily an  $\alpha$  cobalt-tungsten structure. In this condition the ductility should be a much improved solid solution.

The literature concerning wrought alloys indicate these systems require tungsten contents close to 35% in order to achieve the optimum strength. However, when the alloys exceed 30% W, temperatures approaching the theoretical melting point 2700°F are required to adequately dissolve the Co-W intermetallic compounds. A choice of compositions for electroforms, therefore, appeared to be between 25 and 35% tungsten, and solution heat treatment temperatures could be as low as 1900°F. These alloys could also be precipitation hardened by aging at temperatures between 1300 and 1800°F.

## EXPERIMENTAL PROCEDURES AND RESULTS

### I. Experimental Electrodeposition of Various Alloys

All of the various solutions used in these experiments were made up in 2-liter pyrex beakers, heated on a thermostatically controlled hot plate. In all cases the cathode was a .060" x 3" x 4" sheet of platinum. After preparation and visual examination for appearance the deposits were removed from the platinum by appropriate chemical treatment. Analysis for the various elements was then performed, using conventional techniques. Results of these experiments appear in Table I. Figure 25 is a display part coated with the nickel-manganese alloy, item No. 16 of Table I.

### II. Preparation and Testing of Cobalt - Nickel-Tungsten Alloys

#### A. Preparation by Electroforming

A 30-liter capacity polypropylene lined tank was charged with a solution of the following composition and maintained at operating conditions shown on page 12.

		<u>gms/liter</u>
Cobalt Sulfate	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	115
Sodium Tungstate	$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	43
Rochelle Salt	$\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$	380
Ammonium Chloride	$\text{NH}_4\text{Cl}$	50
Nickel Sulfate	$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	5
Triton x -100*		0.5

\*Rohm & Haas Company, 712 Locust St., Philadelphia, Pa.

Additions of nickel, cobalt, and tungsten were made as required, based on a solution analysis every four hours.

pH	- 8 to 9 using ammonia gas bubbled through the solution
Temperature	- 190 $\pm$ 5°F using quartz glass immersion heaters.
Current Density	- 50 amps/sq ft.
Anodes	- cobalt

Tensile specimens as illustrated in Figure 1 were electroformed from this bath by methods described below. Aluminum plates .071" x 6" x 6.5" were masked with neoprene maskant\* in such a manner that only five areas of 1" x 6" of aluminum were exposed. These exposed areas were treated conventionally in zincate, copper strike treated and then plated with approximately .005" of sulfur-free silver.

This mandrel was then immersed in the Co-Ni-W electroforming tank until a thickness of .015" to .030" was achieved. The 1" x 6" areas were separated with a 1/8" strip of maskant so that actual strip electroforms .015" to .030" thick x 1" x 6" were produced. After electroforming the neoprene maskant was peeled from the back side of the aluminum mandrel. The aluminum mandrel was then selectively removed in a 20 ounce/gallon

\*Boray Maskant Co., 11434 South Downey Ave., Downey, Calif.

solution of sodium hydroxide, leaving the electroformed strips with approximately .005" of silver on one side. At this stage the electroforms were quite brittle and it was necessary to exercise care in handling. The silver which had been applied to structurally "back-up" the deposit was subsequently melted off during the solution heat treating (annealing) operation.

In order to relieve the brittle condition and improve appreciably the structural strength of the material by heat treatment, the electroform test coupons were first coated with an aluminum oxide - Elvinol<sup>\*</sup> stop-off fluid. Next the coupons were sealed in a stainless steel envelope, which was flushed with dry argon and evacuated several times to remove the oxygen. The specimen envelope was then placed in a cold furnace and the temperature was raised 500°F an hour until a furnace temperature of 2090°F was reached. They were held at 2090°F for four hours, the furnace was turned off and the electroforms were allowed to cool under argon to room temperature. After annealing and cooling, the strips were placed between .020" x 1" x 6" strips of stainless steel and milled together into standard tensile specimens. Specimens were then aged (tempered) at 1300°F for four hours for improved tensile strength and hardness.

\* E. I. DuPont deNemours & Co., Wilmington 98, Delaware

## B. Mechanical Property Tests

Actual tensile tests were conducted on a 5,000-pound capacity Baldwin Universal Test Machine\*, using a load rate of 90,000 psi/minute. Elongations were measured over a 2" gage length. Results for these tests are shown in Table II. Hardness tests were conducted on a Tukon\*\* microhardness tester using a Knoop indenter and a 500-gram load. See Table III for test results.

## III. Effect of Addition Agents and Stress Reducers in Co-W Alloys

Each of the addition agents was tested in a one-liter standard solution with the following composition and operating conditions:

		<u>gms/liter</u>
Cobalt Sulfate	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	115
Rochelle Salt	$\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$	380
Sodium Tungstate	$\text{NaWO}_4 \cdot 2\text{H}_2\text{O}$	43
Ammonium Chloride	$\text{NH}_4\text{Cl}$	50

pH	- 8 to 9 maintained with $\text{NH}_4\text{OH}$
Anodes	- tungsten
Current density	- 50 amps/sq ft
Agitation	- magnetic stirrer
Temperature	- 160 to 190°F

\* Baldwin-Lima-Hamilton Corp., 940 Simpson St., Eddystone, Pa.

\*\* Wilson Tukon Co., Div. of American Chain & Cable, Bridgeport, Conn.

The various addition agents shown in Table IV were tested in this above standard solution. Actual determination of effectiveness of the various addition agents was performed by electroforming approximately .020" to .030" of Co-W alloy onto a vertical 3/8" steel rod suspended in the one-liter test solution. After the desired thickness had been applied, the electroform coated rod was first examined on a binocular stereoscopic microscope, then sectioned, mounted, and examined on a research metallograph. Figures 2, 3, and 4 show the most significant effects.

#### IV. Melting Point Determination

The apparatus for this test consisted of an electrically heated strip in an inert atmosphere contained by a bell jar. The molybdenum strip heater was cupped to hold a chip of the test alloy. As the power was increased, the temperature was monitored by an L & N optical pyrometer until the melting point was observed. The pyrometer was calibrated against a pure nickel chip with a known melting point. Data for these test results are revealed in Table V.

#### V. Taber\* Abrasion Tests

Wear resistance (abrasion) tests were conducted on a model Number 140 Taber abraser. For comparative data similar materials, i.e., chromium electroplate, stainless steel, and electroformed nickel were also tested. Conven-

\*(Taber Instrument Co., North Tonawanda, N. Y.)

tional Taber abrasion test methods were conducted at room temperature, using a 1,000-gram load, CS-17 wheels. Each test material was exposed to 3 test intervals of 10,000 cycles each. Weight loss in grams was determined after each 10,000-cycle test period. Table VI exhibits test results for Taber abrasive tests.

VI. Air Oxidation Resistance at 1800°F

Data for this test were obtained primarily from the literature cited. One group of data on 72% cobalt - 28% tungsten were obtained in the GD/FW Materials Laboratory. Specimens approximately 15 cm<sup>2</sup> in area were heated in air in a furnace for periods indicated in Table VII. Specimens were weighed, heated, descaled of oxidation products and again weighed to determine loss in weight per unit area. Table VII also contains all the test results for these experiments.

VII. Salt Spray Accelerated Corrosion Test

Data reported in Table VIII was obtained by exposing triplicate specimens .030" x 1" x 1.5" at a 15° from vertical inclination in a 20% salt spray chamber operated as described in Federal Test Method Standard 151, method 811.

VIII. Preparation and Testing of Co-W Alloy Electroforms

A. Experimental Electroforming Solutions

Bath 1

Tensile specimens of a 35% W - 65% Co composition

and the display part shown in Figure 5 were prepared from the following bath:

		<u>gms/liter</u>
Cobalt Sulfate	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	115
Sodium Tungstate	$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	43
Rochelle Salts	$\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$	380
Ammonium Chloride	$\text{NH}_4\text{Cl}$	50
Triton X-100		0.5
pH	- 8 to 9 using ammonia gas bubbled through the solution	
Temperature	- 160 to 190°F	
Current density	- 50 amps/sq ft	
Anodes	- cobalt or tungsten	
Constant Agitation and Filtration		

#### Bath 2

The following bath was used to deposit tensile specimens of a 28% W - 72% Co composition deposit.

		<u>gms/liter</u>
Cobalt Sulfate	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	120
Sodium Tungstate	$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	30
Rochelle Salts	$\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$	380
Ammonium Chloride	$\text{NH}_4\text{Cl}$	50
Barretts S.N.A.P.*		0.5

\* Barrett Chemical Products Company  
Shelton, Connecticut

pH	- 8 to 9 using ammonia gas bubbled through the solution
Temperature	- 160 to 190°F
Current density	- 50 amps/sq ft
Anodes	- cobalt or tungsten

B. Selection of Optimum Conditions for Solution Heat Treating and Tempering

Several specimens were prepared from Bath 2 above (28% W - 72% Co), utilizing mandrel techniques described earlier. Specimens were divided into groups and treated individually at various temperatures in a horizontal tube furnace under a dry argon atmosphere. Specimens were purged in the cool end of the furnace tube, then advanced to the hot zone where they were heated to temperature in approximately 10 minutes. After one hour at temperature the samples were withdrawn to the cool zone and once they had cooled to below 700°F, were removed from the furnace. Solution heat treating temperatures surveyed were 1800°F, 1845°F, 1900°F, 2000°F, and 2100°F. After the various specimens were exposed individually to one of the above conditions they were sectioned and prepared for metallographic examination. From this preliminary study of microstructures the following heat treatments were used on the tensile specimens:

Solution heat treating - 1845°F for 16 hours

Solution heat treating - 2000°F for 16 hours

Aging (tempering) - 1350°F for 16 hours

Aging (tempering) - 1550°F for 8 hours

Photomicrographs showing the metallurgical effects of these various treatments are shown in Figures 6 through 24.

#### DISCUSSION AND CONCLUSIONS

##### I. Experimental Electrodeposition of Various Alloys

Basically, our search was for an alloy satisfying the following requirements.

1. Nickel or cobalt matrix
2. Binary or ternary alloying elements of the refractory metal type
3. A composition providing mechanical properties amenable by heat treatment
4. High temperature oxidation resistance in air
5. Improved hardness and/or wear resistance
6. Balanced electroforming solution capable of deposit composition control and sustained long term operation.

From Table I it is apparent that many varieties of nickel or cobalt matrices are possible. Of course, all of the above listed requirements were not satisfied. In many cases the limiting factor was long term solution electroforming capability. However, several useful

solutions evolved. Solution number 16 (Table I) was used for deposits in the thickness range of ordinary electrodeposits. For deposits greater than that thickness, addition agents and careful solution composition control would be necessary. Solution numbers 3A and 11A were judged to be capable of satisfying most of the above requirements and consequently they were selected for more concentrated development experiments reported later.

## II. Preparation and Testing of Cobalt-Nickel-Tungsten Alloys

Tensile and hardness test specimens were produced and tested. Hardness values from Table III for this material in the solution heat treated - aged condition were superior to electroformed nickel. Both the Co-Ni-W and the Co-W produced hardness as high as Rockwell C53. Tensile properties reported in Table II were somewhat lower than those of electroformed nickel. Two problems were apparent and not solved in these experiments. First, all pitting caused by slight hydrogen gas evolution at the cathode was not eliminated by the Triton X-100 wetting agent (used to lower the solution surface tension). Secondly, the deposit was not completely homogeneous. When examined on a metallograph, a considerable number of microcracks were evident which accounted for the mediocre tensile properties.

### III. Determination of the Effects of Addition Agents and Stress Reducers on Co-W Alloys

In our first work with the Co-W alloys, it was readily apparent that the pitted, brittle deposit would need considerable improvement. Consequently, an industry survey was conducted and then different stress reducers and/or wetting agents were obtained and tested. Almost all of those tested produced some improvement in the deposit. From Table IV and Figures 2, 3, and 4, it is obvious that saccharin and Barrett's S.N.A.P. wetting agents were definite improvements in deposit quality. This material showed marked improvement over Triton X-100 and in later experiments it was responsible for complete elimination of pitting. Although the saccharin appeared to improve deposit integrity, it was not used later since it might increase the likelihood of undesirable sulfur contamination in the deposit.

### IV. Melting Point

The melting point of the 35% W, 65% Co was found to be 2490°F or approximately 200°F below the value reported in the literature. The low melting point may have been caused by bath impurities which were included by the alloy.

### V. Taber Abrasion Tests

Air, sand, rain erosion resistance, as well as ordinary wear resistance, are desirable properties of a material for aerospace environment. Because of the high hardness values

obtained for these materials it was reasonable to assume they would have good wear properties. Specimens of 28% W - 72% Co were Taber abrasion tested along with similar materials such as chromium electroplate, 321 stainless steel and electroformed nickel. From Table V it is apparent that cobalt-tungsten is considerably superior to nickel, the present most commonly used aerospace electroforming material. In fact, it is comparable to 321 stainless steel. However, when compared to chromium electroplate the Co-W alloy has approximately four times the weight loss, due to wear, of chromium. Consequently, it is concluded that Co-W is not a replacement for chromium in wear applications.

#### VI. Air Oxidation Resistance at 1800°F.

One of the most important physical properties of aerospace materials is high temperature air oxidation resistance. There are greater needs and less choices of materials in this area than practically any other. In Table VII, both Battelle and GD/FW data are compared to chromium electroplate and nickel-chromium diffused alloy. In air oxidation resistance at 1800°F the Co-W alloy is inferior to chromium or nickel-chromium diffused alloy.

#### VII. Salt Spray Accelerated Corrosion Tests

Any material having certain aerospace environmental attributes must also have ground service life and perhaps storage capability. In this respect then, the material

should have reasonable corrosion resistance. In Table VIII data are reported for Co-W specimens exposed to 20% salt spray accelerated corrosion environment. From the detailed visual observations made at 50, 100, and 192 hours, it was concluded the Co-W has good corrosion resistance.

#### VIII. Tensile and Hardness Tests for Cobalt-Tungsten Alloys

One of the most important objectives of this program was to develop alloys of good structural strength, particularly with respect to electroformed nickel. Sample and Knapp<sup>11</sup> reported tensile strength for sulfamate nickel to be approximately 115,000 psi at room temperature. In Table IX tensile values as high as 131,268 psi were obtained. Since the electroformed specimens were not completely homogeneous and free from stress-imposed micro-cracks, the writers feel that substantial increases in tensile values are possible.

The specimen having the higher tensile strength had the most satisfactory solution heat treated condition. A survey to determine this optimum metallurgical condition is reported in Figures 6 through 24. Figure 20 exhibits the metallurgical condition of the material having a tensile strength of 131,268 psi. Although a fair amount of inhomogeneity is revealed, the metallurgical condition of the alloy is a tremendous improvement over the material in the as-deposited state, displayed in Figure 6.

## IX. Metallography

Two conditions associated with electroforms are disclosed by the as-deposited microstructure. Slight imperfections on the silver "receiver" sometimes prevent a uniform initiation of the deposit which may then develop a void or a "blossom." If the imperfection is not bridged the void enlarges to become a conically shaped pit with the apex at the imperfection. A blossom forms when the imperfection builds up deposit slightly ahead of the surrounding material. A firm bond with main deposit may never be established and the blossom will grow to the full thickness of the plate. These two discontinuities contribute to the brittleness of the electroform; however, an addition of wetting agent to a well-agitated bath has minimized these two developments.

The second observed condition concerns the inhomogeneity of the deposit. Even with close control of the composition and operation of the bath, the alloy deposits as laminae of various compositions. Two instances of this condition are illustrated by Figure 6; 6A is considered a better deposit than 6B because the laminae are finer, hence more easily homogenized by heat treatment, and the blossoms are less pronounced.

A third condition troublesome during the heat treatment of electroforms is entrapped gas which tends to form blisters. Although not completely resolved, gas blisters are prevented from forming by heating the continuously

evacuated envelope very slowly from room temperature. Nevertheless, internally trapped gases produce a multitude of small voids when the deposit is heated below 2000°F; at 2000°F and above the voids begin to agglomerate and eventually cause blisters in the softened alloy. Some examples of gas voids are shown by Figures 16, 17, and 18.

Samples of two electroform batches were heat treated above and below the theoretical solid solubility limit to determine the optimum solutioning temperature from the microstructure. At 1800°F, Figures 7, 8, and 9 the structure was primarily an  $\epsilon$  -  $\text{Co}_3\text{W}$  phase although some islands of  $\delta$  were beginning to form. As the temperature was raised, more  $\delta$  formed in the lean areas of the deposit, Figures 10 through 15, and at 2000°F the transition to  $\delta\text{-Co}_3\text{W}$  was nearly complete, Figures 16 through 19. The first solution heat treatment was done at 1845°F; the choice between incomplete solution without gas voids and complete solution with gas voids. The mechanical properties were unsatisfactory. The second choice was 2000°F which produced gas voids, but good mechanical properties.

Aging at 1350°F increased the tensile strength from 120 to 131 ksi, the highest strength obtained by the alloy. Figures 20 and 21 show the microstructure to be a decomposed  $\delta$  and  $\epsilon\text{-Co}_3\text{W}$  phases which were fine when compared with the same electroform aged at 1550°F.

From this metallographic study it was concluded that an electrodeposited alloy containing 72% Co - 28% W developed good tensile strengths when it was solution heat treated at 2000°F and aged at 1350°F.

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TABLE I  
EXPERIMENTAL SOLUTIONS FOR  
PRODUCING ELECTROFORMED ALLOYS OF VARIOUS COMPOSITIONS

Solution Number	Ingredients and Concentration	Electroforming Solution - Operating Conditions	Applied Current Density	Composition of Alloy Produced <sup>1</sup>	Appearance of Electroform
1A	CoSO <sub>4</sub> · 7H <sub>2</sub> O - 5 g/l Na <sub>2</sub> WO <sub>4</sub> · 2H <sub>2</sub> O - 65 g/l NH <sub>4</sub> Cl - 50 g/l Na <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> · 2H <sub>2</sub> O - 100 g/l	pH, 8.5 with NH <sub>4</sub> OH Anodes - W Temp - 190±5°F	50 ASF	Co - 49% W - 51%	Fair - darker formation in higher current density areas
1B	Same as 1A	Same as 1A	100 ASF	Co - 44% W - 56%	Same as 1A
2A	CoSO <sub>4</sub> · 7H <sub>2</sub> O - 5 g/l Na <sub>2</sub> WO <sub>4</sub> · 2H <sub>2</sub> O - 130 g/l NH <sub>4</sub> Cl - 50 g/l Na <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> · 2H <sub>2</sub> O - 100 g/l	Same as 1A	50 ASF	Co - 58% W - 42%	Same as 1A
2B	Same as 2A	Same as 2A	100 ASF	Co - 35% W - 65%	Same as 2A
3A	KNaC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> · 4H <sub>2</sub> O - 380 g/l CoSO <sub>4</sub> · 7H <sub>2</sub> O - 115 g/l Na <sub>2</sub> WO <sub>4</sub> · 2H <sub>2</sub> O - 43 g/l NH <sub>4</sub> Cl - 50 g/l	Same as 2A	50 ASF	Co - 66% W - 33%	Good - very slight darker edge effect
3B	Same as 3A	Same as 3A	100 ASF	Co - 58% W - 42%	Same as 3A
4A	CoSO <sub>4</sub> · 7H <sub>2</sub> O - 60 g/l Na <sub>2</sub> WO <sub>4</sub> · 2H <sub>2</sub> O - 130 g/l KNaC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> · 4H <sub>2</sub> O - 380 g/l NH <sub>4</sub> Cl - 50 g/l	Same as 3A	50 ASF	Co - 50% W - 49%	Same as 3A
4B	Same as 4A	Same as 4A	100 ASF	Co - 41% W - 59%	Same as 3A

ERR-FW-217  
Page 28

1 - When composition does not total 100% the difference is due to oxide formation during disposition and the error from one sample analysis. The tungsten is believed higher than reported.

TABLE I  
(Continued)

Solution Number	Ingredients and Concentration	Electroforming Solution - Operating Conditions	Applied Current Density	Composition of Alloy Produced	Appearance of Electroform
5	CoCl <sub>2</sub> · 6H <sub>2</sub> O - 102 g/l Na <sub>2</sub> WO <sub>4</sub> · 2H <sub>2</sub> O - 45 g/l KNaC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> · 4H <sub>2</sub> O - 400 g/l NH <sub>4</sub> Cl - 50 g/l	Same as 4A	50 ASF	Co - 32% W - 67.9%	Fair - Deposit darker and especially so at high current density areas
6A	NaReO <sub>4</sub> - 5 g/100 cc CoSO <sub>4</sub> · 7H <sub>2</sub> O - 5 g/100 cc Na <sub>2</sub> WO <sub>4</sub> · 2H <sub>2</sub> O - 4.3 g/100 cc NH <sub>4</sub> Cl - 5 g/100 cc KNaC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> · 4H <sub>2</sub> O - 38 g/100 cc	Same as 4A	50 ASF	Co - 14% W - 3.3% Re - 82%	Uniform deposit grey-black in color; heavy gassing during electrolysis
6B	Same as 6A	Same as 6A	100 ASF	Co - 2% W - 5% Re - 93%	Same as 6A
7A	CoSO <sub>4</sub> · 7H <sub>2</sub> O - 75 g/l Fe(NH <sub>4</sub> ) <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> · 6H <sub>2</sub> O - 25 g/l Na <sub>2</sub> WO <sub>4</sub> · 2H <sub>2</sub> O - 100 g/l KNaC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> · 4H <sub>2</sub> O - 380 g/l NH <sub>4</sub> Cl - 50 g/l	Same as 6A	50 ASF	Co - 62% W - 38% Fe - 0%	Poor - dark strata around edges
7B	Same as 7A	Same as 7A	100 ASF	Co - 60% W - 40% Fe - 0%	Poor - dark strata over most of specimen
8A	CoSO <sub>4</sub> · 7H <sub>2</sub> O - 75 g/l NiSO <sub>4</sub> · 6H <sub>2</sub> O - 15 g/l Na <sub>2</sub> WO <sub>4</sub> · 2H <sub>2</sub> O - 100 g/l KNaC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> · 4H <sub>2</sub> O - 380 g/l NH <sub>4</sub> Cl - 50 g/l	Same as 7A	50 ASF	Co - 18% Ni - 62% W - 15%	Uniform, dull grey color

TABLE I  
(Continued)

Solution Number	Ingredients and Concentration	Electroforming Solution - Operating Conditions	Applied Current Density	Composition of Alloy Produced	Appearance of Electroform
8B	Same as 8A	Same as 8A	100 ASF	Co - 6% Ni - 60% W - 30%	Same as 8A
9A	CoSO <sub>4</sub> · 7H <sub>2</sub> O - 50 g/l Na <sub>2</sub> WO <sub>4</sub> · 2H <sub>2</sub> O - 100 g/l Na <sub>2</sub> MoO <sub>4</sub> · 2H <sub>2</sub> O - 100 g/l KNaC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> · 4H <sub>2</sub> O - 380 g/l NH <sub>4</sub> Cl - 50 g/l	Same as 8A	50 ASF	Co - 4% W - 43% Mo - 50%	Uniform, black deposit
9B	Same as 9A	Same as 9A	100 ASF	Co - 2% W - 17% Mo - 80%	Same as 9A
10A	CoSO <sub>4</sub> · 7H <sub>2</sub> O - 115 g/l Na <sub>2</sub> WO <sub>4</sub> · 2H <sub>2</sub> O - 43 g/l KNaC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> · 4H <sub>2</sub> O - 380 g/l NH <sub>4</sub> Cl - 50 g/l NiSO <sub>4</sub> · 6H <sub>2</sub> O - 1 g/l	Same as 9A	50 ASF	Co - 68% Ni - 5% W - 20%	Uniform, dull grey color
11A	CoSO <sub>4</sub> · 7H <sub>2</sub> O - 115 g/l Na <sub>2</sub> WO <sub>4</sub> · 2H <sub>2</sub> O - 43 g/l KNaC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> · 4H <sub>2</sub> O - 380 g/l NH <sub>4</sub> Cl - 50 g/l NiSO <sub>4</sub> · 6H <sub>2</sub> O - 5 g/l Triton X-100 - 0.5 g/l	Same as 10A	50 ASF	Co - 76% Ni - 8% W - 21%	Same as 10B
11B	Same as 11A	Same as 11A	100 ASF	Co - 67% Ni - 5% W - 26%	Same as 11A

TABLE I  
(Continued)

Solution Number	Ingredients and Concentration	Electroforming Solution - Operating Conditions	Applied Current Density	Composition of Alloy Produced	Appearance of Electroform
12A	CoSO <sub>4</sub> · 7H <sub>2</sub> O - 115 g/l Na <sub>2</sub> WO <sub>4</sub> · 2H <sub>2</sub> O - 43 g/l KNaC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> · 4H <sub>2</sub> O - 380 g/l NH <sub>4</sub> Cl - 50 g/l NiSO <sub>4</sub> · 6H <sub>2</sub> O - 15 g/l	Same as 11A	50 ASF	Co - 65% Ni - 7% W - 6.7%	
12B	Same as 12A	Same as 12A	100 ASF	Co - 65% Ni - 7% W - 20%	
13	CuCN KNaC <sub>4</sub> H <sub>4</sub> O <sub>6</sub> · 4H <sub>2</sub> O - 10 g/l NiCl <sub>2</sub> · 6H <sub>2</sub> O - 10 g/l KOH - 5 g/l KCN - 15 g/l NH <sub>4</sub> OH Q.S. to pH of 10	Temp - 120°F Anodes - Platinum pH - 10 adjusted with NH <sub>4</sub> O <sub>4</sub>	288 ASF	Ni - 20% Cu - 80%	Dull grey black, good adhesion to copper basis metal
14	MnSO <sub>4</sub> · H <sub>2</sub> O - 75 g/l (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> - 56 g/l NH <sub>4</sub> CNS - 45 g/l NiSO <sub>4</sub> - 60 g/l NiCl <sub>2</sub> · 6H <sub>2</sub> O - 7.5 g/l H <sub>3</sub> BO <sub>3</sub>	Temp - 170°F pH - 4 to 6 (adjusted with NH <sub>4</sub> OH) Anode - Carbon Rod	120 ASF	Ni - 96.6% Mn - 3.4%	Dull grey black, deposit somewhat brittle
15	MnSO <sub>4</sub> · H <sub>2</sub> O - 380 g/l NiSO <sub>4</sub> · 6H <sub>2</sub> O - 1-5 g/l (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> - 75 g/l	Temp - Room Anodes - Nickel	5 ASF	3.6 to 4.0% Manganese Balance Nickel	Brittle, cracked, Spalling deposit Short bath life
16	NiSO <sub>4</sub> · 6H <sub>2</sub> O - 16.5 g/l MnSO <sub>4</sub> · H <sub>2</sub> O - 125 g/l (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> - 75 g/l	pH 6, adjusted with NH <sub>4</sub> OH Temp - room Anodes - bagged nickel	15-30 ASF optimum 25 ASF	Mn - 4.76% Ni - 95.24%	Smooth, uniform, bright deposit, good adhesion to nickel electroform. No apparent cracks or spalling of deposit. Shown in Fig. 25.

TABLE II  
RESULTS OF TENSILE TESTS AT ROOM TEMPERATURE  
FOR 5% NICKEL, 65% COBALT AND 30% TUNGSTEN ELECTROFORMS

Solution Heat Treated 2090°F - 4 Hours; Aged 1300°F for 4 Hours

Specimen No.	Thickness	Width	Area	Ultimate * Load (lbs)	Ultimate Strength PSI
1	.0125	.495	.00619	322	52,103
2	.0144	.486	.00699	358	51,126
3	.0150	.486	.00729	340	46,639
4**	.0208	.497	.01036	350	34,660
Average 1, 2 & 3					49,623

\* Specimens had no yield strength and zero elongation.

\*\* Specimen failed at apparent crack outside 2" gage mark.

TABLE III

RESULTS OF HARDNESS MEASUREMENTS ON 5% N1,  
30% TUNGSTEN, 65% COBALT ELECTROFORMS

500-Gram Load		10.25 Lens	.4582 Factor
Determination No.	Metallurgical Condition	Knopp No.	Converted Rockwell C
1	As Electroformed	462.7	45
2		462.7	45
3		557	51
4		599	53
5		599	53
6		588	52+
7		588	52+
8		511	48
Average		545.9	49
1	Solution Heat Treated 2090°F for 4 hours	261.3	22
2		333.8	33
3		320.5	31
4		274.5	24
5		320.5	31
6		329.3	32
7		324.8	32
8		292.4	27
9		232.1	20
Average		298.8	28
1	Solution Heat Treated and Aged (Tempered) 2090°F - 4 hours 1300°F - 4 hours	455.4	44
2		462.7	45
3		529	49
4		610	54
5		599	53
6		578	52
7		494	47
Average		532.5	49

TABLE IV

EFFECTS OF ADDITION AGENTS ON PITTING AND  
STRESS IN Co-W ELECTROFORMS

Addition Agent and Test Condition	Results - Improvement in Homogeneity and Surface Uniformity
<p>1. <u>Control Specimen</u> Approximately .020" to .030" of Co-W was electroformed onto a 3/8" steel rod using the following solution and operating condition:</p> <p>CoSO<sub>4</sub>.7H<sub>2</sub>O - 115 g/l NaWO<sub>4</sub>.2H<sub>2</sub>O - 43 g/l KNaC<sub>4</sub>H<sub>4</sub>O<sub>6</sub>.4H<sub>2</sub>O - 380 g/l NH<sub>4</sub>Cl 50 g/l</p> <p>pH - adjusted 8-9 with NH<sub>4</sub>OH Anodes - W Temp - 160-190°F Current Density - 50ASF Agitation - None</p>	<p>Slightly large grain deposit, darker at bottom 1/2" of basis metal rod. Pit frequency was approximately one per sq in, somewhat greater along top surface of the electroforming solution.</p>
<p>2. <u>Effects of Solution Agitation</u> (Identical solution and test conditions in #1) Moderate agitation using a prop type agitator.</p>	<p>Slight improvement in color and smaller grain size. No real improvement in pitting problem.</p>
<p>3. <u>Effects by Adding 0.2 g/l Saccharin to a Solution</u> Identical to No. 1 Moderate agitation with magnetic stirrer.</p>	<p>Improved brightness and grain size. No improvement in pitting problem.</p>
<p>4. <u>Addition of .35% by weight Naccanol N.R.* to a solution</u> identical to number one. With moderate circulation by a magnetic stirrer.</p>	<p>Good color, uniformity and brightness. Photomicrograph reveals a undesirable grain growth. Complete elimination of pits.</p>
<p>5. <u>.25% Magnus** N.W. 3</u> to agitated solution #1</p>	<p>Pits on extreme bottom end. many dark grey to brown spots on most of surface. Somewhat darker in high current density area. Improved grain size.</p>

\* Allied Chemical Corporation  
National Aniline Division  
42 Rector St.  
New York, N. Y.

\*\*Magnus Chemical Co.  
3 Kreie St.  
Garwood, N. J.

TABLE IV (Cont'd)

Addition Agent and Test Condition	Results - Improvement in Homogeneity and Surface Uniformity
6. .5% Triton X-123* To agitated solution #1	Improved color and grain size. Pit problem only partially eliminated.
7. 0.1% Triton X-100* To agitated solution #1	Occassional pit but almost complete pit suppression. Good color, uniformity and improved small grain size.
8. .037% Barretts** Sulfamate Nickel and Pit Agent (S.N.A.P.) to agitated solution #1	Occasional pit, good color, uniformity and small grain size.
9. 0.2% S.N.A.P. to agitated solution #1	No pits. Improved throwing power. Good color and grain size. Lustrous in area of maximum agitation.
10. 0.5% S.N.A.P. to agitated solution #1	No pits. Improved luster and color. Good fine grain structure with almost no edge effect. This particular wetting agent and concentration was subsequently chosen for all solutions used in preparing test specimens.
11. 0.75% S.N.A.P. to agitated solution #1	No pits, unusually good brightness at edges. Good color and grain size.

\* Rohm & Haas Co.  
712 Locust St.  
Philadelphia 5, Pa.

\*\*Barrett Chemical Products Co., Inc.  
5 Bridge St.  
Shelton, Connecticut

TABLE V  
MISCELLANEOUS TEST DATA FOR  
VARIOUS COBALT-TUNGSTEN ALLOYS

A. Melting Point (35% W - 65% Co) --- 2490°F  
B. Hardness (35% W - 65% Co)

<u>Metallurgical Condition of Alloy</u>	<u>Rockwell C Hardness</u>
1. As-deposited	46-51
2. Annealed 2 hrs at 2050°F (inert atm.)	27-31
3. Annealed 2 hrs at 2050°F plus 1.5 hrs age at 1300°F	43-52

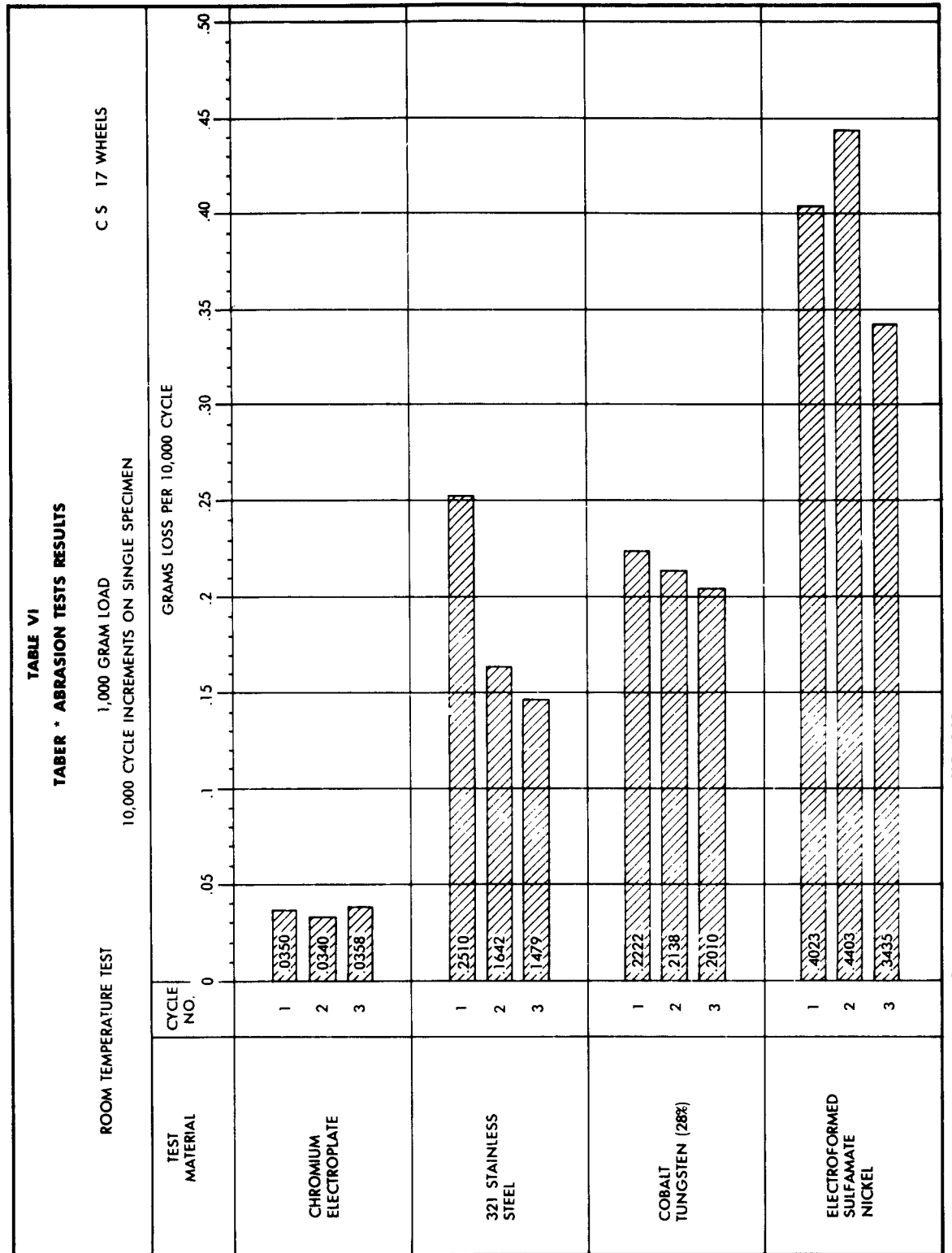


TABLE VII

AIR OXIDATION RESISTANCE OF VARIOUS METALS AT 1800°F

Electrodeposited Metal Or Alloy	Rate in Air at 1800°F in mg/cm <sup>2</sup> /hour		
	<u>Exposure Period</u>		
	<u>8 Hours</u>	<u>10 Hours</u>	<u>100 Hours</u>
Nickel-Chromium (diffused alloy layer)*		0.35	0.1b
Chromium <sup>1</sup>		0.70	0.28
73% Co - 27% Tungsten Electroform <sup>1</sup>		5.8	2.8
72% Co - 28% Tungsten** Electroform	6.5		
	6.7		
	5.7		

\* W. H. Safranek and G. R. Schafer, "Properties of Electrodeposits at Elevated Temperatures", Proceedings of The American Electroplaters Society (106, 1956)

\*\* Tests performed in the Materials Laboratory, General Dynamics/  
Fort Worth.

TABLE VIII

EFFECTS OF 20% SALT SPRAY ON Co-W (28%) ELECTROFORMS

I. Results:

A. Visual Observations at the 50-Hour Period:

Specimens were approximately 20% covered with a thin film of rust-colored corrosion products.

B. Observations at the 100-Hour Period:

Test specimens were approximately 50% covered with a thin film of reddish-brown corrosion products.

C. Observations at the 192-Hour Period:

Corrosion products of greenish-brown color covered 60% of the test specimen area.

Note: The type of corrosion observed was surface oxidation with no evidence of pitting or intergranular corrosion.

TABLE IX

TENSILE TESTS OF VARIOUS COBALT-TUNGSTEN ALLOYS

A. Room Temperature Tests

<u>% W in Alloy</u>	<u>Solution Heat Treat Condition</u>	<u>Temper Condition</u>	<u>Ultimate* Tensile Strength (psi)</u>	<u>Number of Specimens Tested per Group</u>
28	2000°F - 16 hours	None	119,760	2
28	2000°F - 16 hours	1350°F - 16 hrs.	131,268	2
28	2350°F - 1 hour	None	62,885	5
28	2350°F - 1 hour	1300°F - 12 hrs.	27,100	2
28	2350°F - 1 hour	1500°F - 12 hrs.	43,045	2
35	2050°F - 2 hours	None	92,500	2
35	2050°F - 2 hours	1300°F - 1.5 hrs.	106,600	2

\* Maximum values obtained from specimens which were not completely homogeneous, free from gas pockets and microcracks. Specimens had no appreciable elongation.

B. Elevated Temperature Tests at 1300°F\*

28	2000°F - 16 hours	1350°F - 16 hrs.	10,680	1
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\* Heated at 1300°F for 30 minutes prior to test.

FIGURE 1  
ELECTROFORMED TENSILE SPECIMENS OF  
60% NICKEL, 35% COBALT, 30% TUNGSTEN  
ALLOY



THICKNESS .015"

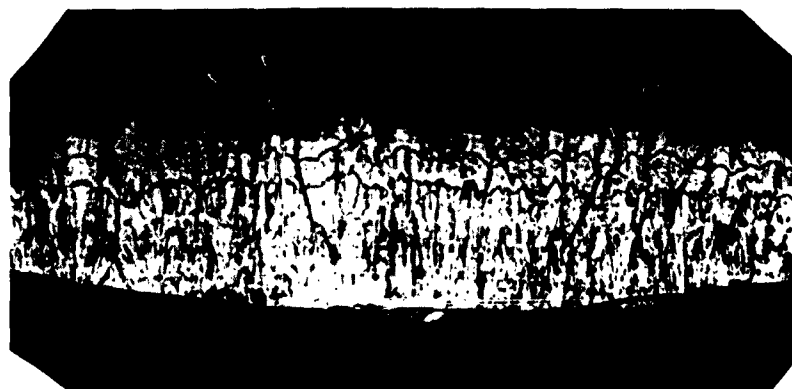


FIGURE 2

MAG. 250X

SN 6521

LNH\*

Microsection of a Control Specimen. No agitation, no wetting agent added.



FIGURE 3

MAG. 250X

SN 6523

LNH

Agitation with Saccharin used as a Stress Reducer. Improved color, reduced grain size. No reduction in pit formations.

\* Etchant - 80% Lactic, 10% Nitric, 10% Hydrogen Peroxide

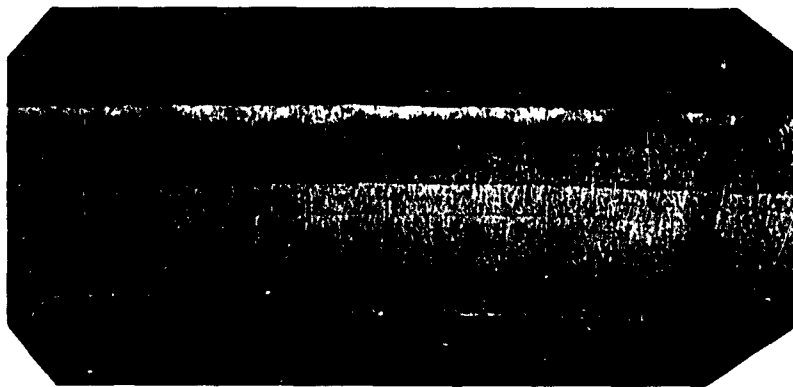


FIGURE 4

MAG. 250X

SN 6520

LNH

Agitation with Addition of 1% Barretts S.N.A.P.

Improved grain size, homogeneity. Unusual good brightness and complete eliminating of pitting.

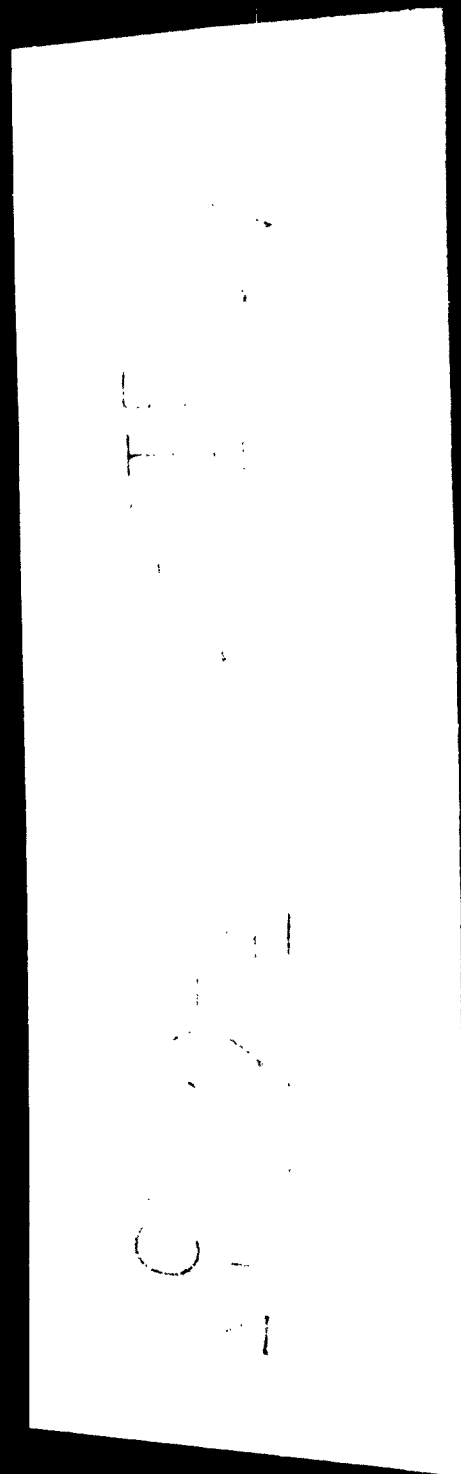


FIGURE 5



FIGURE 6

MAG. 150X

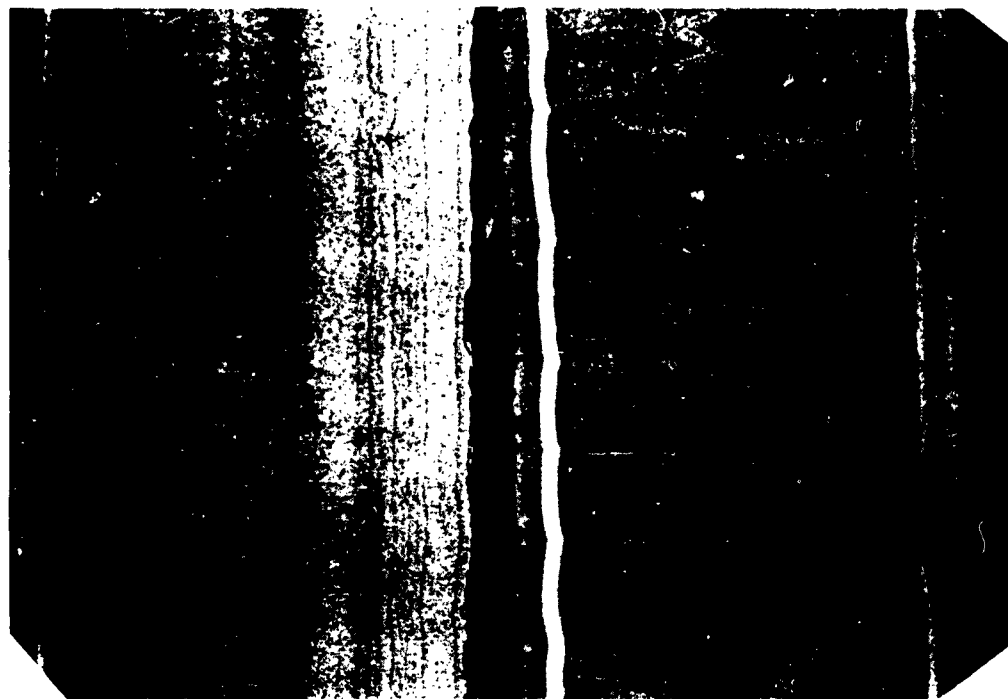
6851

LNH

B

A

Specimens as deposited. The laminated structure of the A was deposited uniformly except for the bands near each edge. It was deposited from a new solution. The structure of B exhibited small voids and fissures. It was deposited in a fourth group of specimens and appears to be less uniformly deposited than A.



MAG. 150X

FIGURE 7  
SN 6848

LNH

B

A

Specimens heat treated at 1800°F for 1 hour. After this treatment the A sample was adjudged to be the more homogenous deposit. The "fern-like"  $\epsilon$  -  $\text{Co}_3\text{W}$  is seen in both specimens but it is more pronounced in the B.

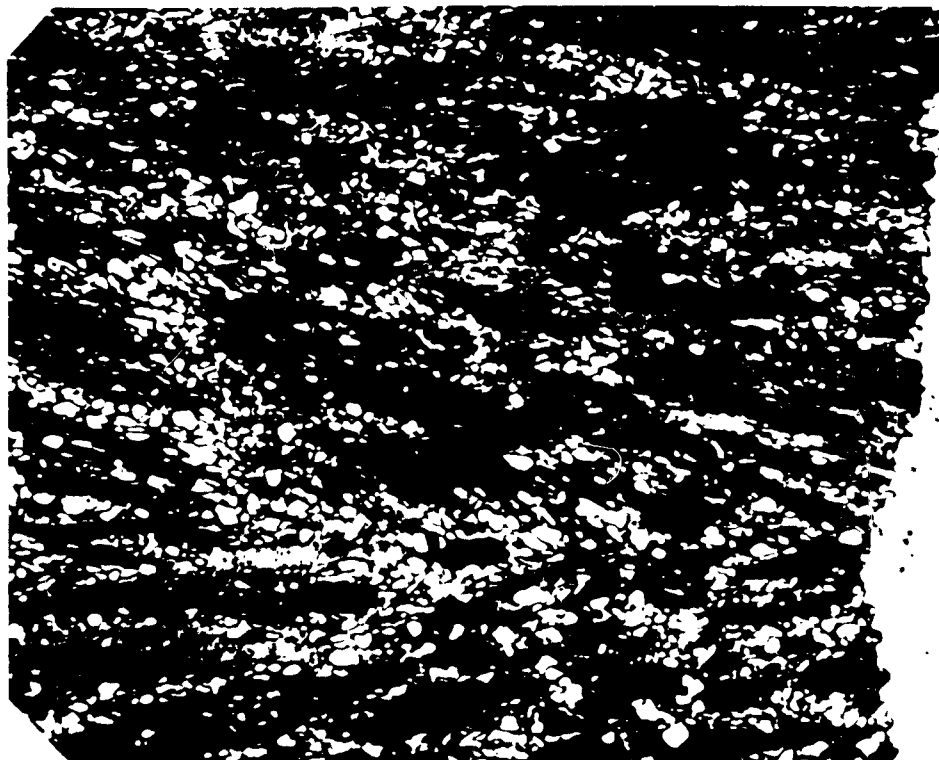


FIGURE 8

MAG. 2000X

6854

LNH

Specimen A, Heat Treated (Ht) @ 1800°F for 1 hr.

"Ferns" of  $\epsilon$  -  $\text{Co}_2\text{W}$  surrounding islands of  $\delta$  in an area near the initial deposit. The white area, right, is the black band seen in Figure 6 and thought to be primarily  $\delta$ .



FIGURE 9

MAG. 2000X

6855

LNH

Specimen B, Ht @ 1800°F for 1 hr.

The "Ferns" of  $E$ -Co<sub>3</sub>W surrounded by islands of  $\epsilon$  in the area of initial deposit. The leaner final deposit is primarily  $\epsilon$  (see Figure 6).

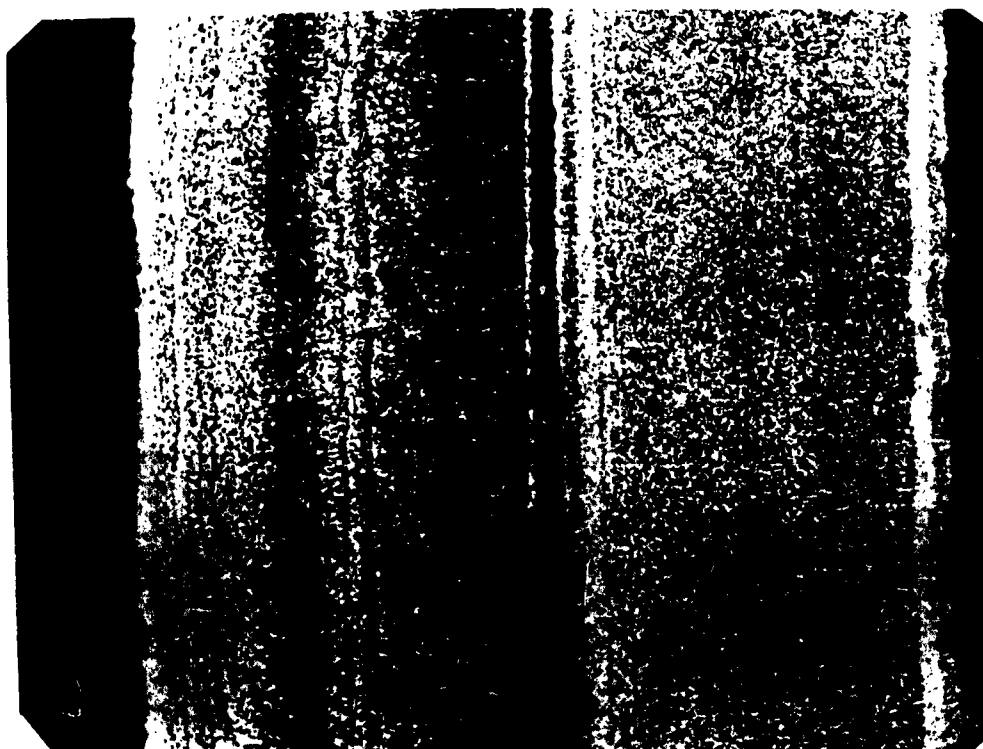


FIGURE 10

MAG. 150X

6870

LNH

B

A

Specimens heat treated at 1845°F for 16 hours. Temperature was not in the  $\alpha$  region of the Co W phase diagram, so that the structure was primarily  $\epsilon$ -Co<sub>3</sub>W, partially spheroidized in A and "ferns" in B. The B sample shows a greater variation in composition than the A.



FIGURE 11

MAG. 2000X

6871

LNH

"A" Sample

A matrix of  $\alpha$  with  $\epsilon$ -Co<sub>3</sub>W particles. (See Figure 10).  
Solution heat treated @ 1845°F for 16 hours.

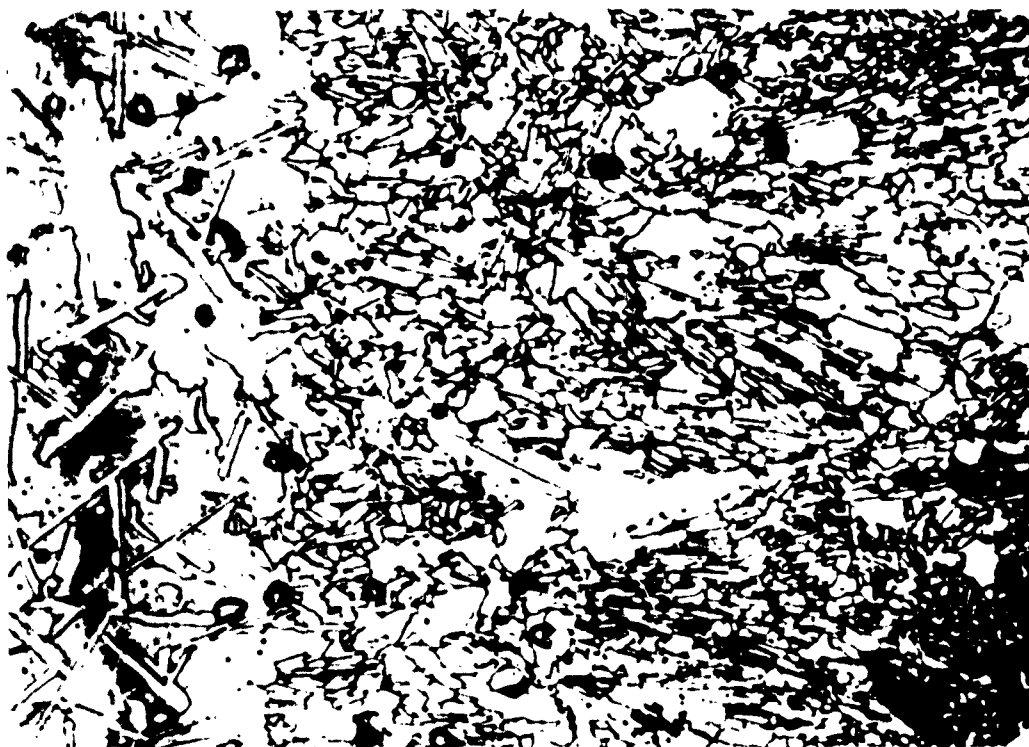


FIGURE 12

MAG. 2000X

6874

LNH

Sample B (Middle)

"Fern" of  $\epsilon$ -Co<sub>3</sub>W are deteriorating to form  $\delta$ . (See Figure 10). SHT @ 1845°F for 16 hours.

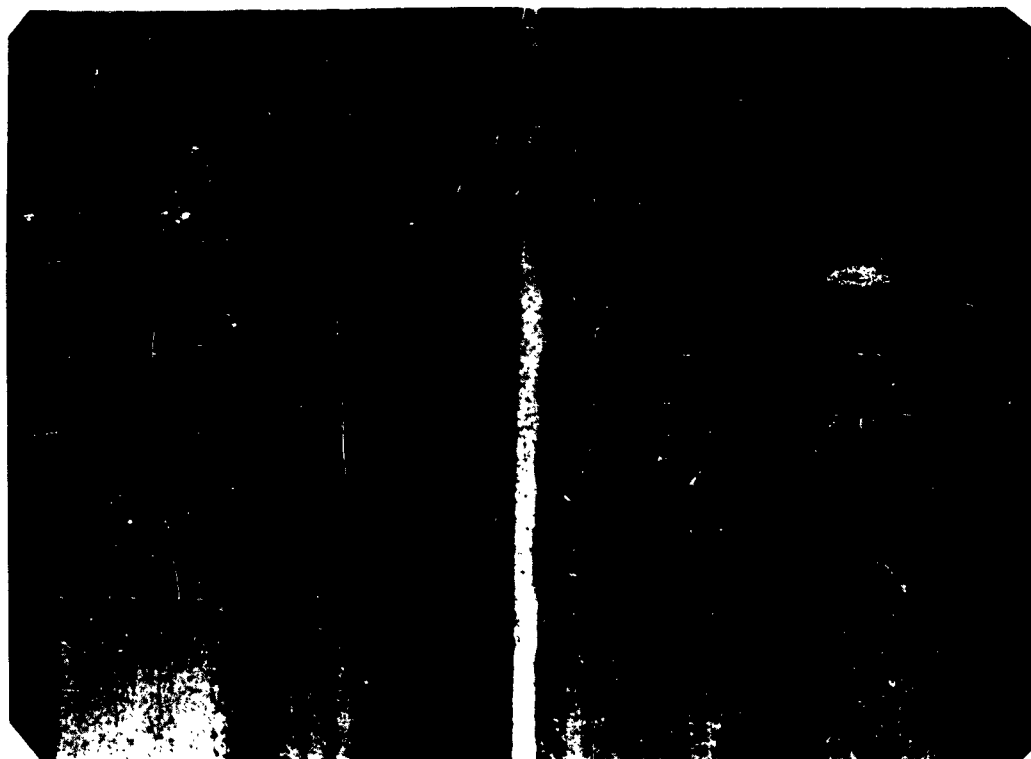


FIGURE 13

MAG. 150X

6849

LNH

B

A

Specimens heat treated at 1900°F for 1 hr.

Both specimens show a transitional  $\epsilon$  phase preparatory to the formation of  $\delta$ . Note gas holes concentrated between the laminae of the B sample.

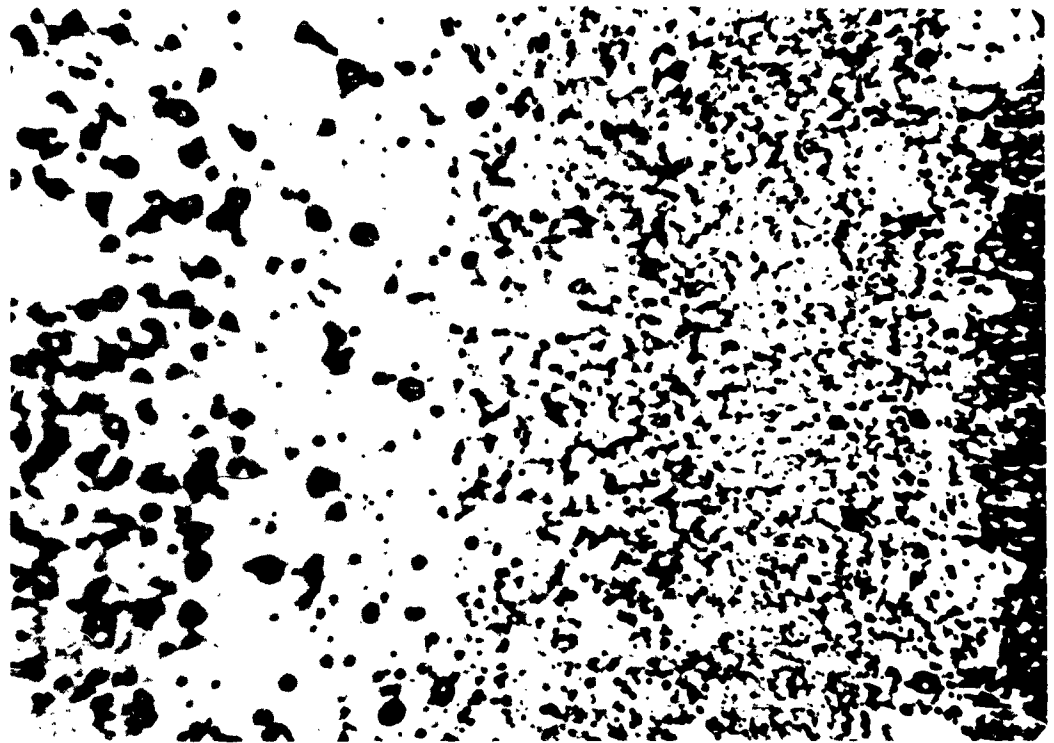


FIGURE 14

MAG. 2000X

6856

LNH

Specimen A Ht @ 1900°F for 1 hr.

In this specimen only a fringe of  $\epsilon$ -Co<sub>3</sub>W is visible in the initial deposit (right). The dark band, now grey, shows some substructure and is filled with small gas voids. On the left is the  $\delta$  matrix with its multitudinous voids of various sizes. These are voids and not particles even though they appear bright, a reflection from the bottom of the hole.

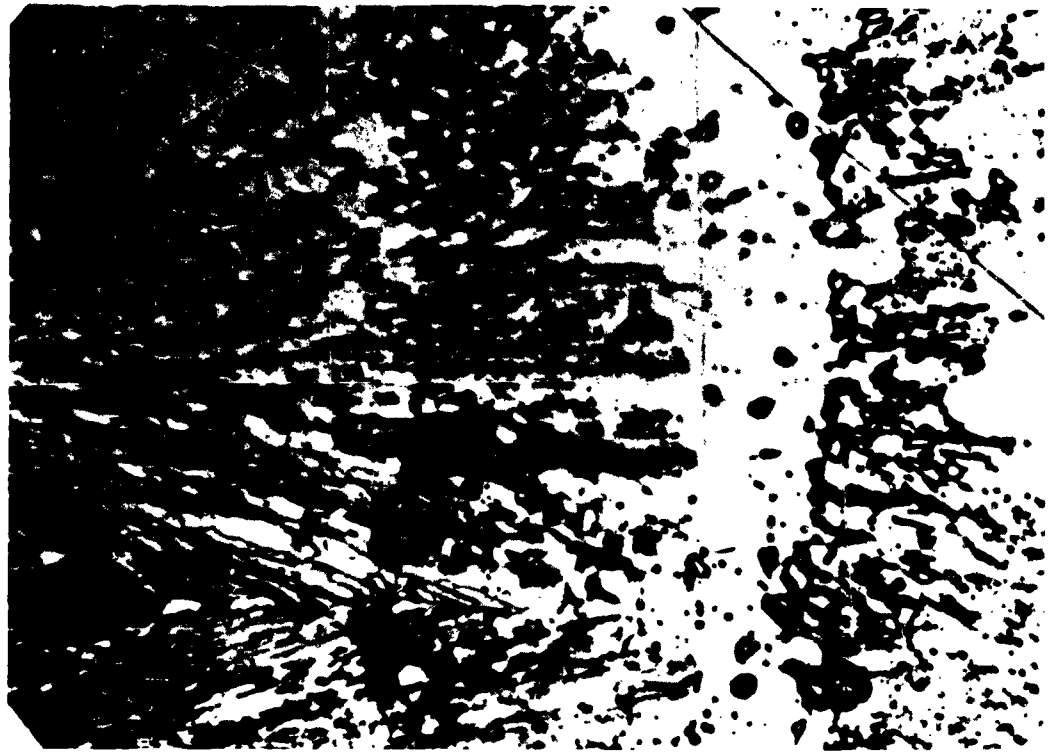


FIGURE 15

MAG. 2000X

6857

LNH

Specimen B, HT @ 1900°F for 1 hr.

"Ferns" of  $\epsilon$ - $\text{Co}_3\text{W}$  are dissolving. Gas voids may be seen between the laminae.

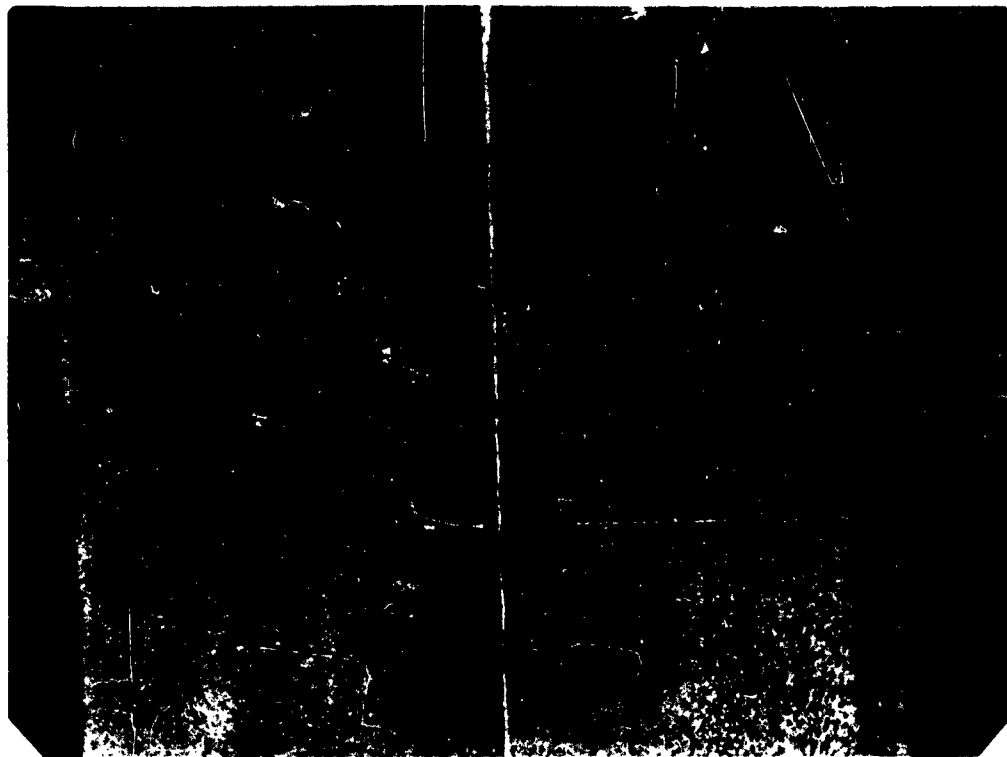


FIGURE 16

MAG. 150X

6850

LNH

B

A

Specimens heat treated at 2000°F for 1 hr.

Some substructure is beginning to appear in the lean areas of the plate. Gas voids are agglomerating in the A sample; some of these have filled with silver through openings to the surface. In the B sample the voids are more dispersed but still lie in between former lamellae.

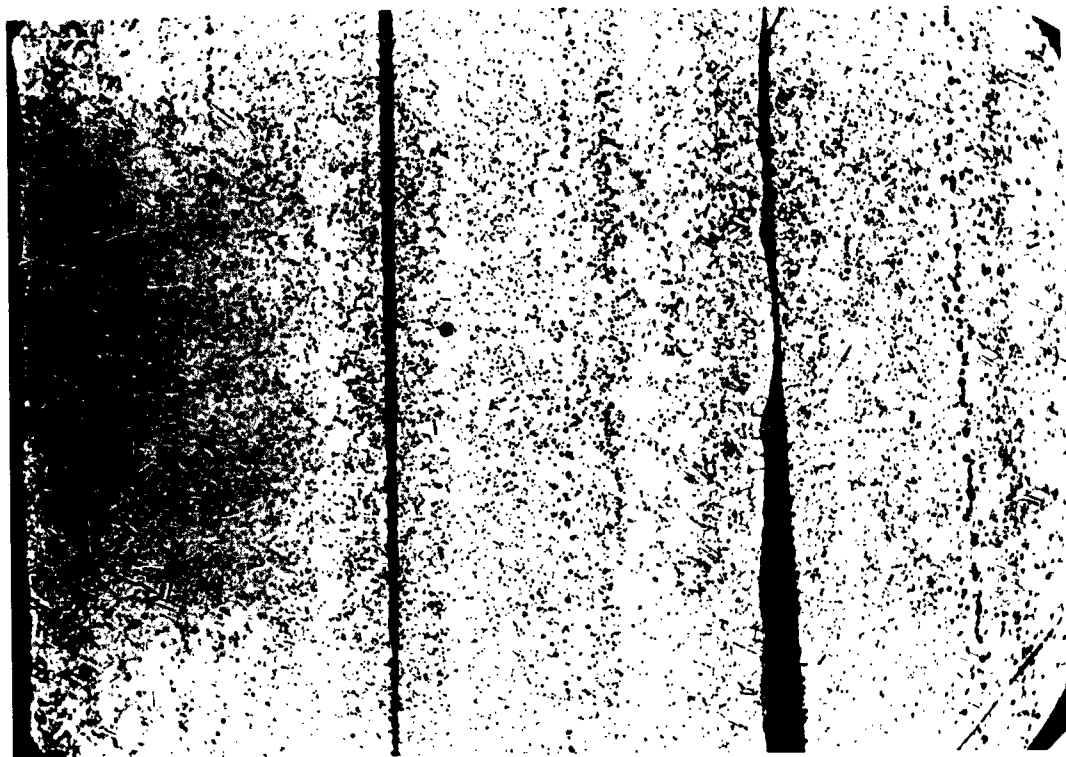


FIGURE 17

MAG. 150X

6877

LNH

Test Specimens After Heat Treatment at 2000°F for 16 Hours

Three pieces of test specimens after solution heat treating at 2000°F for 16 hours. Gas voids appear to have formed in between deposited layers. Basic structure shows almost complete transformation of  $\epsilon$  to  $\alpha$  Co<sub>3</sub>W.

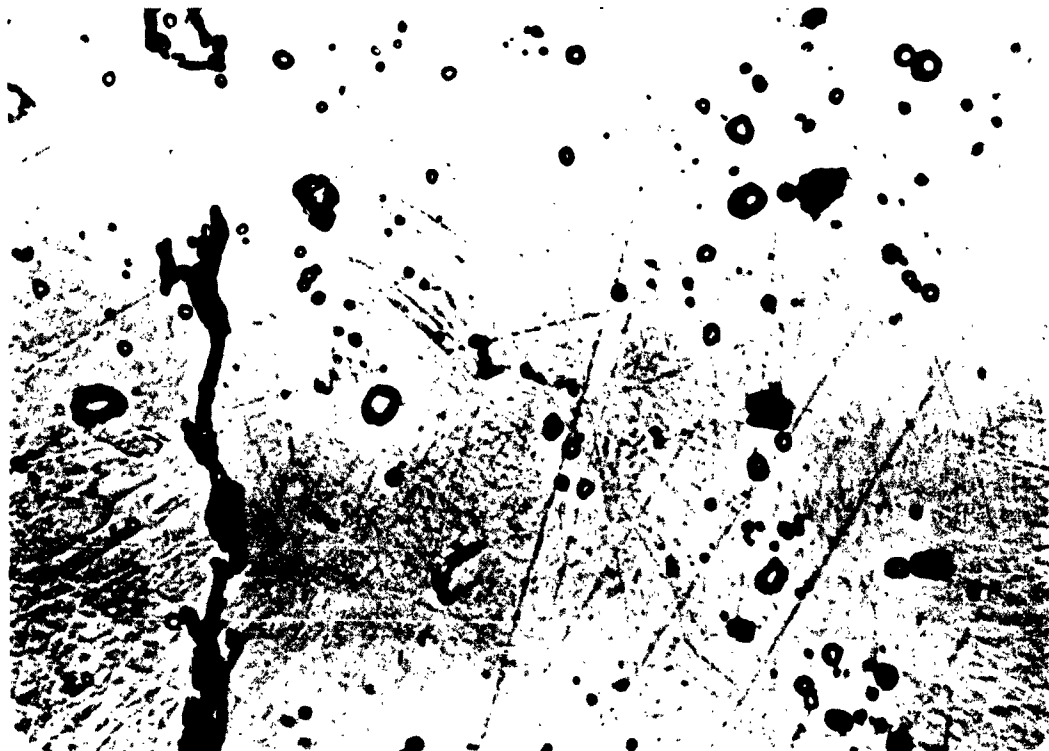


FIGURE 18

MAG. 2000X

6878

LNH

Gas voids at higher magnification. Near the middle of the specimen the voids agglomerated and in some cases joined to form a chain. Co-W alloy heat treated at 2000°F for 16 hours.

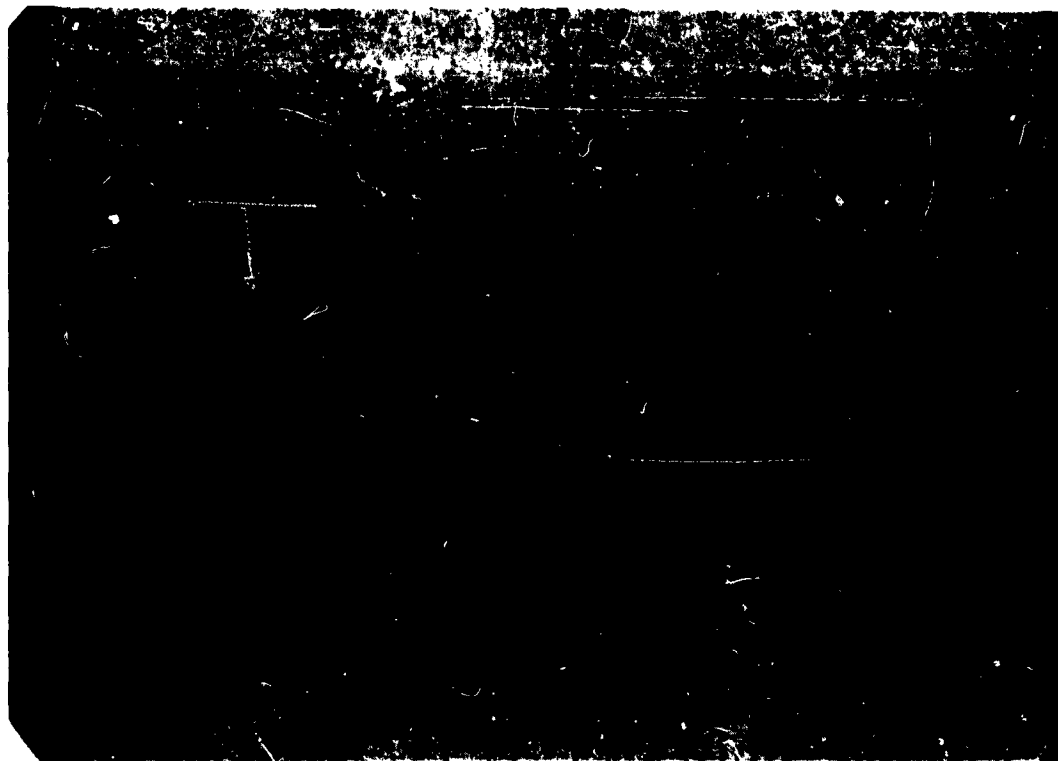


FIGURE 19

MAG. 150X

6914

LNH

Test Specimens Heat Treated at 2000°F for 16 hrs.

The last envelope of test specimens was heat treated at 2000°F for 16 hours. These samples show the typical structure which consists of  $\delta$  and  $\epsilon$ -Co<sub>3</sub>W filled with gas voids and a few cracks. The cracks probably formed during deposition and did not heal during the heat treatment.

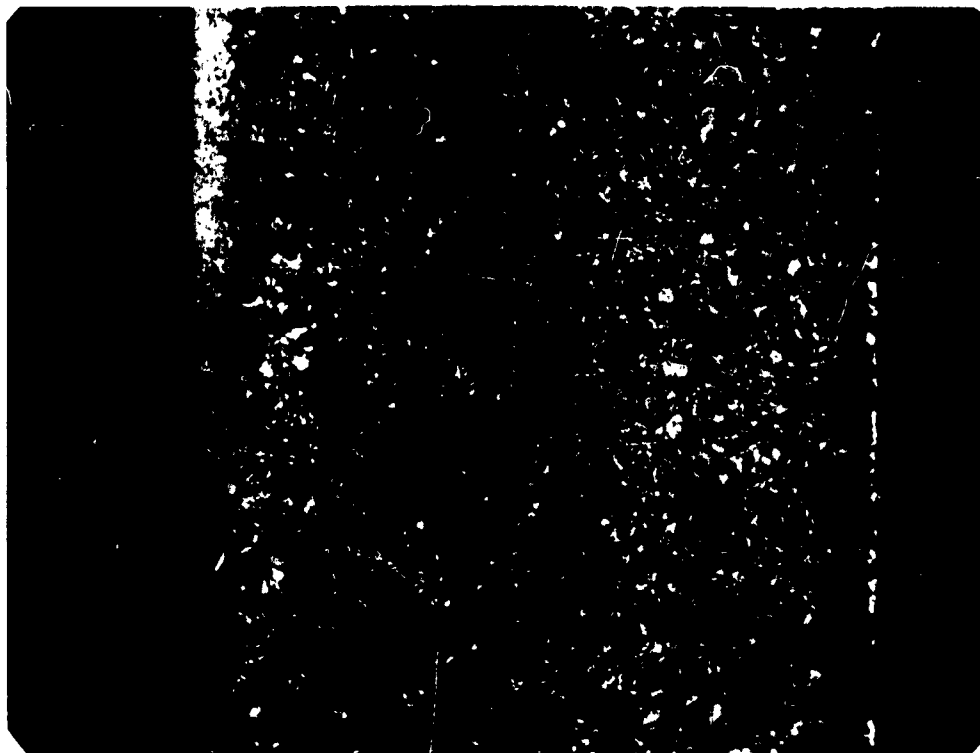


FIGURE 20

MAG. 150X

6928

LNH

Test Specimens Heat Treated at 2000°F for 16 Hours And  
Aged at 1350°F for 16 Hours

A sample of the tensile test specimens solution heat treated at 2000°F for 16 hours and aged at 1350°F for 16 hours. The structure is decomposed  $\alpha$  and  $\epsilon$ -Co<sub>3</sub>W. The result of non-uniform deposition composition shows in this aged structure.

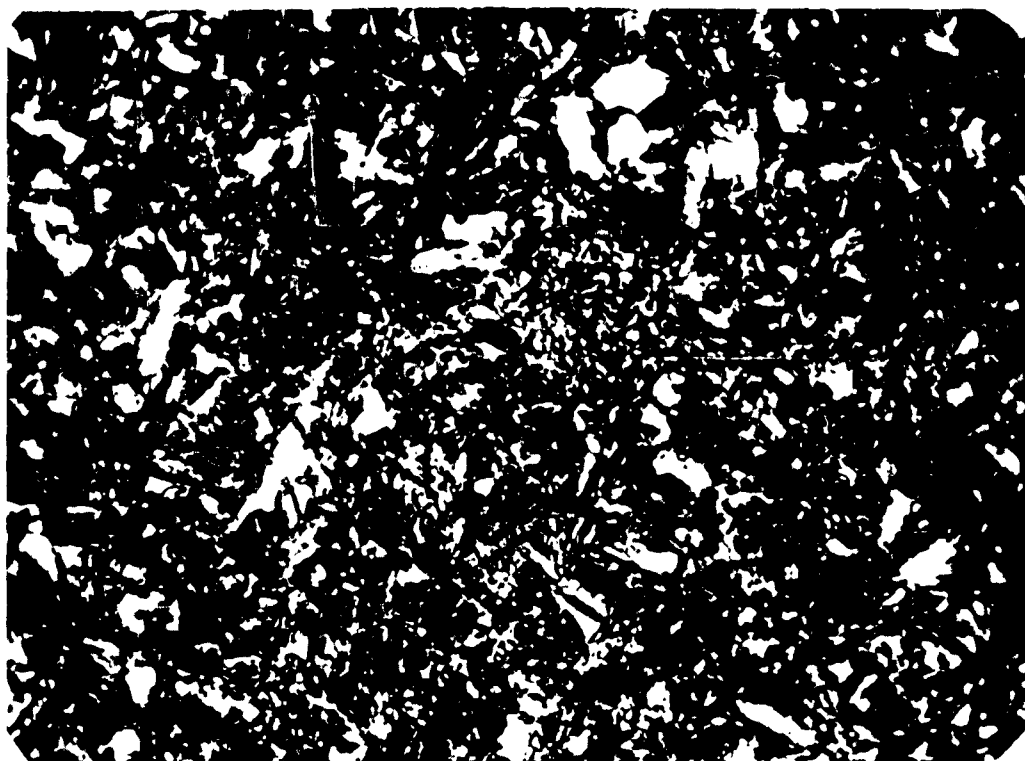


FIGURE 21

MAC. 2000X

6930

LNH

Structure of Co-W Alloy Aged at 1350°F for 16 Hours

Aging the Co-W alloy at 1350°F for 16 hours produced a structure of decomposed  $\zeta$  and  $\epsilon$ -Co<sub>3</sub>W.

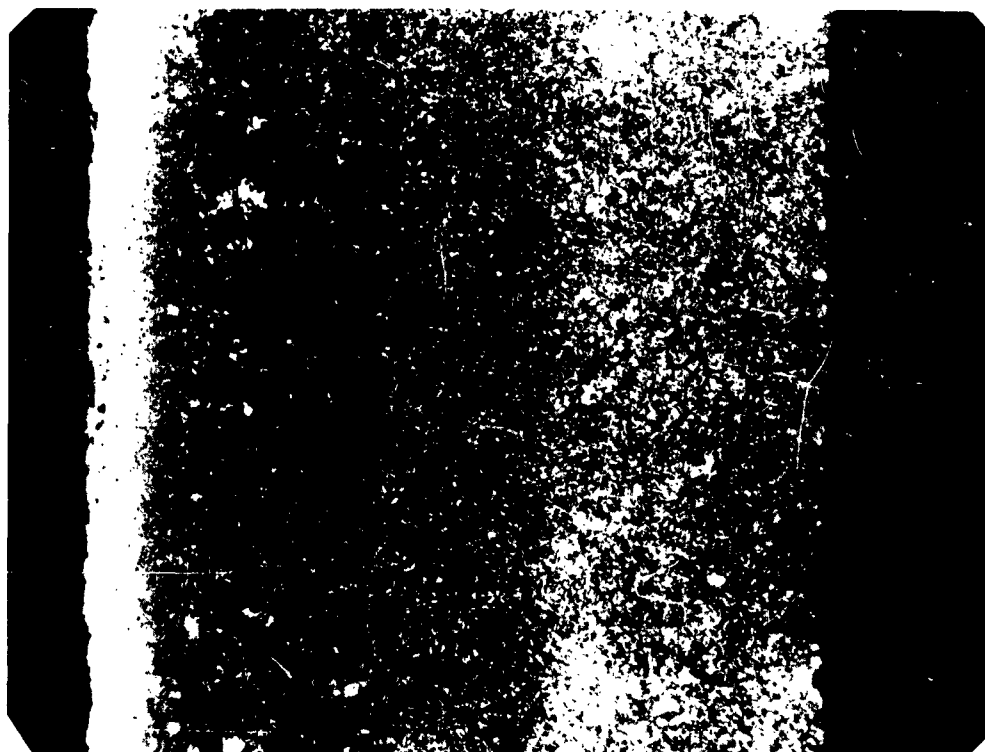


FIGURE 22

MAG. 150X

6929

LNH

Specimen Heat Treated at 2000°F for 16 hours and Aged at 1550°F for 8 Hours.

A sample of the tensile test specimens solution heat treated at 2000°F for 16 hours and aged at 1550°F for 8 hours. The structure shows a partial spheroidization of the  $\epsilon$ -Co<sub>3</sub>W phase and a partial formation of Widamanstätten  $\epsilon$  and  $\epsilon$ -Co<sub>3</sub>W.

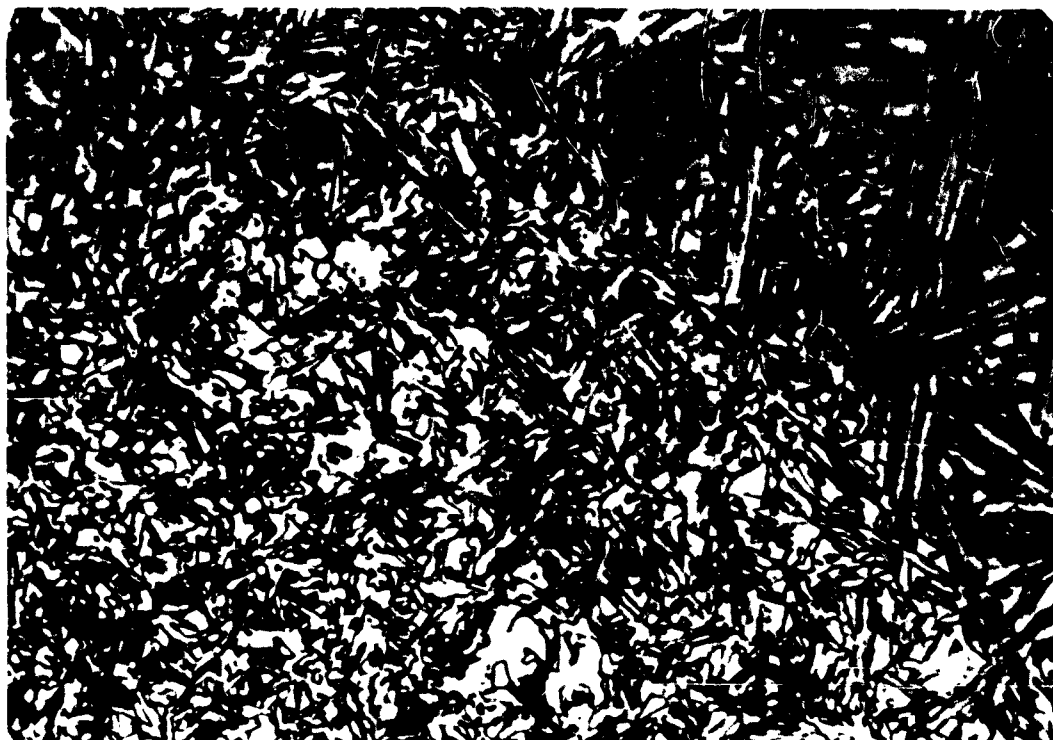


FIGURE 23

MAG. 2000X

6931

LNH

Widamanstätten  $\epsilon$  and Coarse  $\epsilon$ -Co<sub>3</sub>W

Aging the Co-W alloy at 1550°F for 8 hours produced some Widamanstätten  $\epsilon$  and some coarse  $\epsilon$ -Co<sub>3</sub>W. The nonuniformity of the structure is attributed to variations in the composition of the electroplating solution.

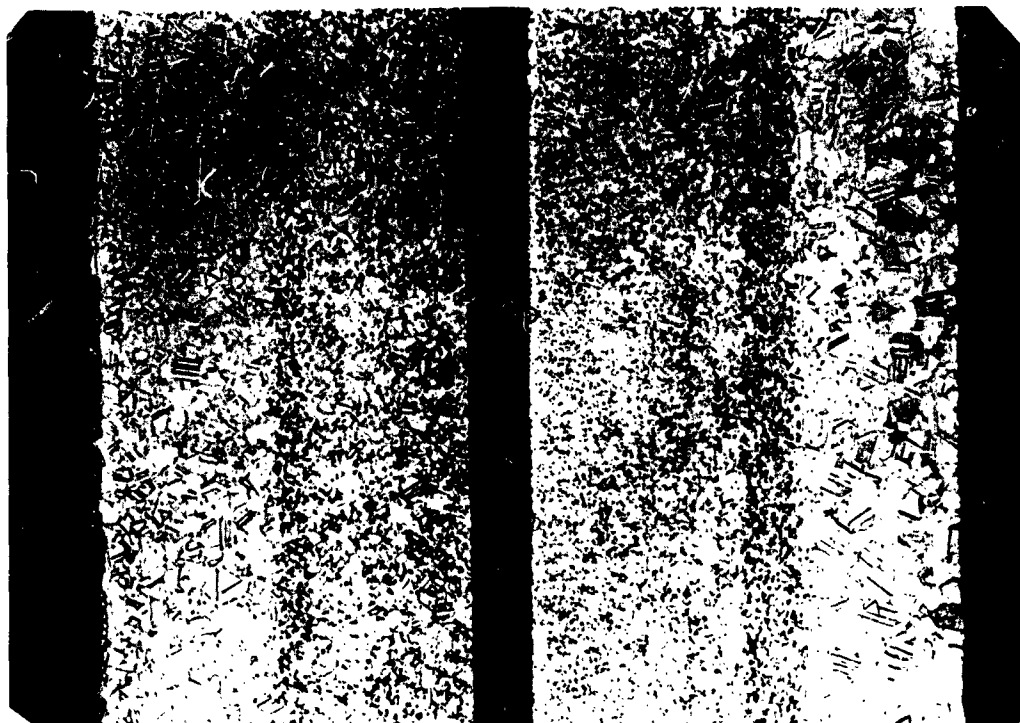


FIGURE 24

MAG. 150X

6852

LNH

A

B

Specimens heat treated at 2100°F/1 hr.

The annealing twins in the  $\alpha$  phase area are clearly seen in both samples. There has been little change in the gas voids although fewer are shown here by comparison with those at 2000°F.

